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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 September 2001 (27.09.2001)

PCT

(10) International Publication Number
WO 01/70472 A1

- (51) International Patent Classification⁷: **B27K 3/32**, 3/22, 3/16
- (74) Agent: **GRIFFITH HACK**; 509 St Kilda Road, Melbourne, VIC 3004 (AU).
- (21) International Application Number: **PCT/AU01/00325**
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (22) International Filing Date: 23 March 2001 (23.03.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
PQ 6449 24 March 2000 (24.03.2000) AU
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
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- Published:
— with international search report
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



WO 01/70472 A1

(54) Title: **PRESERVING COMPOSITIONS**

(57) Abstract: The specification describes wood preserving compositions comprising basic aqueous solutions of zinc and boron compounds. In particular the specification describes wood preserving compositions comprising zinc borate dissolved in aqueous ammonia. Other preservatives such as copper and quaternary ammonium compounds may also be included. Wood impregnated with the preservative composition is resistant to leaching.

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PRESERVING COMPOSITIONS

The present invention relates to preserving compositions for porous products, especially wood.

5 Compounds of boron have been used in the preservation of wood for a number of years. However, one of the difficulties experienced in use of these compounds is their propensity to leach from the substrate into which they have been impregnated. Consequently, compounds of
10 boron have not been particularly useful in preserving timber exposed to water, for example, pylons embedded in a sea bed.

 Basic zinc compounds also have toxic efficacy with respect to wood destroying organisms, both in the
15 marine and land environments. However, despite this efficacy having been known, basic zinc compounds have not been used commercially.

 The present invention is based on the discovery that a composition comprising a basic zinc compound and a
20 compound of boron has a toxic efficacy to wood destroying organisms, both in the marine and land environments with the added benefit of a reduction in the rate at which the boron compound leaches from the impregnated substrate.

 Accordingly, the present invention provides a
25 preserving composition which includes a basic zinc compound and a compound of boron.

 A preferred composition comprises zinc ions and borate ions in an aqueous solution of ammonia. The zinc ions may be derived from any soluble zinc compound and the
30 borate ions may be derived from any soluble borate but zinc borate is preferred. Examples of soluble zinc compounds include zinc sulfate and zinc chloride and examples of soluble borates include sodium borate and potassium borate. A solution of zinc ions and borate ions
35 in aqueous ammonia may be prepared by dissolving zinc borate in an aqueous solution of ammonia at a temperature of about 66°C. Alternatively, a soluble zinc salt may be

- 2 -

combined with a soluble borate salt in an aqueous ammonia solution at a temperature of about 66°C.

The preserving composition of the present invention may be combined with other additives having efficacy as
5 preservatives. These include copper sulfate, fluorides such as potassium fluoride and quaternary ammonium compounds.

Porous compounds, especially porous cellulosic compounds, may be impregnated with the preserving
10 composition of the present invention by flooding the porous compound at reduced pressure. Preferably, the pressure is reduced to a level in the range between 0.5 kPa and 0.9 kPa.

In a further aspect, the present invention
15 provides a means of impregnating a substrate with a preserving composition by means of coacervation. Coacervation occurs when a liquid compound separates into two phases below a particular temperature. One phase is rich in one compound and the other is leaner. Coacervation
20 is similar to crystallisation from a mother liquor.

The following examples illustrate the invention.

EXAMPLE 1

25 Preparation of Impregnant

- 1000 grams of ammonia solution (28%) was added to 1000 grams of water.
- With constant agitation using a magnetic stirrer, 222.5 grams of zinc borate were added to the diluted ammonia
30 solution.
- The solution was heated gently at 66°C to form a clear solution.

Preparation of Wood Blocks

- 35 ◦ *Pinus radiata* clear sapwood was used for the impregnation, and all the wood blocks were conditioned

- 3 -

to less than 15% moisture level.

- The numbered blocks prepared for the impregnation were: 028, 107, 147, 282 and 307.
- The volume of the blocks was measured and the results are given below. Although the volume of each block varies slightly, the volume of every individual block was measured to ensure the accuracy of retention calculated.

10

Block No.	028	107	147	282	307
Volume ($\text{m}^3 \times 10^{-6}$)	12.675	12.521	12.649	12.684	12.848

- The weight of the blocks was determined

Impregnation

- Once a vacuum of 0.9 kPa was reached, the vacuum pump was kept running for 30 minutes, and the lowest vacuum achieved before flooding was 0.65 kPa.
- Flooding was commenced under vacuum.
- Vacuum was released to atmospheric pressure.
- Atmospheric pressure was employed for 60 minutes.
- The solution was sucked back to the work vessel under vacuum at the end of the pressure period.
- Vacuum was applied to the pressure vessel containing the treated blocks.
- After a vacuum of 2.5 kPa was reached, the vacuum was run for 30 minutes.
- The lowest vacuum reached was 2.1 kPa before the vacuum was released.
- The weight of blocks was determined, and the uptake and retention of chemicals calculated. The results are as follows.

30

Block No.	107	307	028	282	147
Uptake (g)	7.7165	9.0291	8.3166	8.084	7.8495
Retention	616.28	702.76	656.14	637.34	620.56

(kg/m³)

- Blocks were dried naturally in the open air.

Leaching

- The leaching was conducted as detailed in the American
5 Wood Preserver's Association Standard E11-8.
- The blocks were impregnated with distilled water in
exactly the same way as in the impregnation with
preservatives.
- Once a vacuum of 1.5 kPa was reached, the vacuum pump
10 was kept running for 30 minutes, and the lowest vacuum
achieved before flooding was 1.3 kPa.
- Distilled water was used for the flooding.
- Vacuum was released to atmospheric pressure.
- The amount of water used was 50 ml per block, and the
15 total amount of water used was 300 ml. The loss of
water to the uptake was re-added.
- Once the leaching was commenced, the leachant was
changed at intervals of 6 hours, 24 hours and every 48
hours afterwards, and the leachates were collected for
20 analysis.

Analysis of Impregnant, Leachates and Digested Blocks after Leaching

- All the analyses were carried out using
- 25 techniques of AAS (Atomic Absorption Spectrometry) and ICP-
AES (Inductively Coupled Plasma-Atomic Emission
Spectrometry) with the final results based on ICP analysis.

1. Analysis of impregnant

- 30 • The impregnant was diluted to an appropriate
concentration that is within the working range of the
analytical instrument.
- The diluted impregnant was determined and the
concentrations of boron and zinc are 12.07g/L and
35 27.89g/L respectively.
- The determined concentration of the impregnant was used

- 5 -

to calculate the mass balance.

2. Analysis of leachates

- The leachates were analysed directly without any further sample preparation.
- The concentrations of boron and zinc in the leachates are as follows.

10

Sample	L1	L2	L3	L4	L5	L6	L7	L8	L9
B (ppm)	204	192	202	107	62.5	48.3	37.4	29.7	26.6
Zn (ppm)	113	90.7	93.9	16.5	16.9	14.0	13.4	9.80	9.35

3. Analysis of digested wood blocks

- Four out of five blocks were used for the digestion and analysis, and the other one was used for penetration test.
- The four blocks were quantitatively powdered, homogenised and dried at 100°C for 2 hours before analysis.
- 3.0000 grams of wood powder were taken for the digestion.
- The digestion was carried out based on the American Wood Preserver's Association Standard A7-93 using nitric acid, sulfuric acid and perchloric acid.
- The solutions obtained from the digestion were analysed for boron and zinc and the results are as follows.

- 6 -

Block No.	028	107	147	307
B in digestion solution (ppm)	197	153	147	219
Total B in each block (mg)	55.23	44.66	43.74	57.13
Zn in digestion solution (ppm)	770	729	744	858
Total Zn in each block (mg)	215.7	212.7	217.2	224.1

Summary of Results

B	Total boron uptake	397.2 mg
	Total boron in wood	200.8 mg
	Boron mass fraction in wood	0.479
	Total boron in leachate	218.1 mg
	Boron mass fraction in leachate	0.521
	Mass balance	105.5 %
	Boron retention after leaching	3.96 kg/m ³
Zn	Total zinc uptake	918.0 mg
	Total zinc in wood	869.7 mg
	Zinc mass fraction in wood	0.906
	Total zinc in leachate	90.61 mg
	Zinc mass fraction in leachate	0.094
	Mass balance	104.6%
	Zinc retention after leaching	17.16 kg/m ³

5

Comment

Overloading could have been committed resulting in a relatively high mass fraction of boron being leached out. The impregnation procedure followed the Bethell full-cell schedule. The severe overloading occurred and some boron leached as a consequence of excess preservative compound being present within the vessels.

10

The boron retention after leaching, however, is still very high, 3.66 kg/m³, compared with 1 kg/m³ required

by an American company.

EXAMPLE 2

5 Preparation of Impregnant

The impregnant used in Example 2 was prepared in the same way as in Example 1.

- 1000 grams of ammonia solution (28%) was added to 1000 grams of water.
- 10 • With constant agitation using a magnetic stirrer, 222.5 grams of zinc borate were added to the diluted ammonia solution.
- The solution was heated gently at 66°C to form a clear solution.

15

Preparation of Wood Blocks

- Very similar procedure to that in Example 1 was used to prepare the blocks.
- The numbered blocks prepared for the impregnation were:
20 062, 100, 206, 223 and 239.
- The volume and the moisture of the blocks were measured.
- The weight of the blocks was determined.

Impregnation

- 25 While the impregnation was conducted in a similar way to that in Example 1, different vacuums were used.

- Once a vacuum of 2.1 kPa was reached, the vacuum pump was kept running for 30 minutes, and the lowest vacuum achieved before flooding was 1.9 kPa.
- 30 • Flooding was commenced under vacuum.
- Vacuum was released to atmospheric pressure after flooding completed.
- Atmospheric pressure was employed for 60 minutes.
- The solution was sucked back to the work vessel under
35 vacuum at the end of the pressure period.
- Vacuum was applied to the pressure vessel containing the treated blocks.

- 8 -

- After a vacuum of 2.5 kPa was reached, the vacuum was run for 30 minutes.
 - The lowest vacuum reached was 2.3 kPa before the vacuum was released.
- 5 ◦ The weight of blocks was determined, and the uptake and retention of chemicals calculated. The results are as follows.

Block No.	062	100	206	223	239
Uptake (g)	8.8483	5.4833	8.0169	6.9345	8.2680
Retention (kg/m ³)	702.86	433.94	629.96	553.03	663.35

- 10 ◦ Blocks were dried naturally in the open air.

Leaching

The leaching was carried out in a similar way to that in Example 1 except different vacuums were used.

- 15 ◦ The leaching was conducted as detailed in the American Wood Preserver's Association Standard E11-8.
- The blocks were impregnated with distilled water in exactly the same way as in the impregnation with preservatives.
- 20 ◦ Once a vacuum of 1.6 kPa was reached, the vacuum pump was kept running for 30 minutes, and the lowest vacuum achieved before flooding was 1.4 kPa.
- Distilled water was used for the flooding.
- Vacuum was released to atmospheric pressure.
- 25 ◦ The amount of water used was 50 ml per block, and the total amount of water used was 300 ml. The loss of water to the uptake was re-added.
- Once the leaching was commenced, the leachant was changed at intervals of 6 hours, 24 hours and every 48
- 30 hours afterwards, and the leachates were collected for analysis.

Analysis of Impregnant, Leachates and Digested Blocks after Leaching

All the analyses were carried out using techniques of AAS (Atomic Absorption Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) with the final results based on ICP analysis.

1. *Analysis of impregnant*

- The impregnant was diluted to an appropriate concentration that is within the working range of the analytical instrument.
- The diluted impregnant was determined and the concentrations of boron and zinc are 11.30g/L and 28.28g/L respectively.
- The determined concentration of the impregnant was used to calculate the mass balance.

2. *Analysis of leachates*

- The leachates were analysed directly without any further sample preparation.
- The boron concentrations in the leachates are as follows.

Sample	L1	L2	L3	L4	L5	L6	L7	L8	L9
B (ppm)	236	170	68.1	40.4	29.4	25.3	21.9	20.6	17.3

3. *Analysis of digested wood blocks*

- Four out of five blocks were used for the digestion and analysis, and the other one was used for penetration test.
- The four blocks were quantitatively powdered, homogenised and dried at 100°C for 2 hours before analysis.
- 3.0000 grams of wood powder were taken for the digestion.
- The digestion was carried out based on the American Wood Preserver's Association Standard A7-93 using nitric

- 10 -

acid, sulfuric acid and perchloric acid.

- The solutions obtained from the digestion were analysed for boron and zinc and the results are as follows.

Block No.	100	206	223	239
B in digestion solution (ppm)	85.3	166	118	165
Total B in each block (mg)	24.14	47.42	34.16	47.31
Zn in digestion solution (ppm)	556	724	672	741
Total Zn in each block (mg)	157.5	206.3	193.9	212.9

5

Summary of Results

B	Total boron uptake	324.2 mg
	Total boron in wood	153.0 mg
	Boron mass fraction in wood	0.504
	Total boron in leachate	150.9 mg
	Boron mass fraction in leachate	0.496
	Mass balance	93.74 %
	Boron retention after leaching	3.04 kg/m ³
Zn	Total zinc uptake	811.7 mg
	Total zinc in wood	770.6 mg
	Zinc mass fraction in wood	0.949
	Total zinc in leachate	
	Zinc mass fraction in leachate	
	Mass balance	
	Zinc retention after leaching	15.30 kg/m ³

Comment

10

Overloading could have been committed resulting in a relatively high mass fraction of boron being leached out. The impregnation procedure followed the Bethell full-cell schedule. The severe overloading occurred and some boron leached as a consequence of excess preservative

- 11 -

compound being present within the vessels.

The boron retention after leaching, however, is still very high, 3.04 kg/m³, compared with 1 kg/m³ required by an American company.

5

EXAMPLE 3

Preparation of Impregnant

While the formulation used in this example is different
10 from that used in Examples 1 and 2, the preparation of the impregnant was commenced in the similar way to that in Examples 1 and 2.

- 1000 grams of ammonia solution (28%) was added to 1000 grams of water.
- 15 • With constant agitation using a magnetic stirrer, 222.5 grams of zinc borate were added to the diluted ammonia solution.
- The solution was heated gently at 66°C to form a clear solution.
- 20 • 200 grams of copper sulfate were added gradually and then the solution was cooled to room temperature.

Preparation of Wood Blocks

Same procedures were used to prepare blocks as that used in
25 Examples 1 and 2.

- The numbered blocks prepared for the impregnation were: 043, 044, 190, 211 and 245.
- The volume and the moisture of the blocks were measured.
- The weight of the blocks was determined.

30

Impregnation

While the impregnation was conducted in a similar way to that in Examples 1 and 2, different vacuums were used.

- Once a vacuum of 1.9 kPa was reached, the vacuum was
35 maintained for 30 minutes, and the vacuum before flooding was also 1.7 kPa.
- Flooding was commenced under vacuum.

- 12 -

- Vacuum was released to atmospheric pressure after flooding completed.
- Atmospheric pressure was employed for 60 minutes.
- The solution was sucked back to the work vessel under vacuum at the end of the pressure period.
- Vacuum was applied to the pressure vessel containing the treated blocks.
- After a vacuum of 2.4 kPa was reached, the vacuum was run for 30 minutes.
- The lowest vacuum reached was 2.3 kPa before the vacuum was released.
- The mass of blocks was determined straight after the pressure treatment, and the uptake and retention of chemicals calculated. The results are as follows.

Block No.	043	044	190	211	245
Uptake (g)	7.8235	8.2008	8.3631	7.2498	7.3124
Retention (kg/m ³)	617.58	638.19	659.65	576.98	579.43

- Blocks were dried naturally in the open air and conditioned for two weeks.
- NOTE: The vacuum utilised in this modified Bethell schedule is very important and we have discovered this to be a significant part of this process, ultimately aimed at reduced boron leaching.

Leaching

- The leaching was carried out in a similar way to that in Examples 1 and 2 although different vacuums were used.
- The leaching was conducted as detailed in the American Wood Preserver's Association Standard E11-8.
 - The blocks were impregnated with distilled water in exactly the same way as in the impregnation with preservatives.
 - Once a vacuum of 1.5 kPa was reached, the vacuum pump was kept running for 30 minutes.

- 13 -

- Distilled water was used for the flooding.
- Vacuum was released to atmospheric pressure.
- The amount of water used was 50 ml per block, and the total amount of water used was 300 ml. The loss of water to the uptake was re-added.
- Once the leaching was commenced, the leachant was changed at intervals of 6 hours, 24 hours and every 48 hours afterwards, and the leachates were collected for analysis.

10

Analysis of Impregnant, Leachates and Digested Blocks after Leaching

All the analyses were carried out using techniques of AAS (Atomic Absorption Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) with the final results based on ICP analysis.

1. *Analysis of impregnant*
 - The impregnant was diluted to an appropriate concentration that is within the working range of the analytical instrument.
 - The diluted impregnant was determined and the concentrations of boron, zinc and copper were 10.80g/L, 26.94g/L and 36.52g/L respectively.
 - The determined concentration of the impregnant was used to calculate the mass balance.
2. *Analysis of leachates*
 - The leachates were analysed directly without any further sample preparation.
 - The concentrations of boron and copper in the leachates were as follows.

30

Sample	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10
B (ppm)	377	221	92.0	53.0	37.3	5.37	13.1	9.66	8.50	5.25
Cu (ppm)	32.9	14.2	6.61	5.11	5.17	1.66	2.26	1.86	1.60	1.97

- 14 -

3. *Analysis of digested wood blocks*

- Four out of five blocks were used for the digestion and analysis, and the other one was used for a penetration test.
- 5 • The four blocks were quantitatively powdered, homogenised and dried at 100°C for 2 hours before analysis.
- 3.0000 grams of wood powder were taken for the digestion.
- 10 • The digestion was carried out based on the American Wood Preserver's Association Standard A7-93 using nitric acid, sulfuric acid and perchloric acid.
- The solutions obtained from the digestion were analysed for boron, zinc and copper and the results are as follows.
- 15

Block No.	043	044	190	211
B in digestion solution (ppm)	63.9	52.5	50.2	43.7
Total B in each block (mg)	18.22	16.89	16.00	14.28
Zn in digestion solution (ppm)	475	542	540	414
Total Zn in each block (mg)	135.4	174.3	172.2	135.3
Cu in digestion solution (ppm)	?	1092	1144	920
Total Cu in each block (mg)	108.6	351.3	364.9	300.5

Summary of Results

B	Total boron uptake	341.7 mg
	Total boron in wood	65.38 mg
	Boron mass fraction in wood	0.249
	Total boron in leachate	197.2 mg
	Boron mass fraction in leachate	0.751
	Mass balance	76.84 %
	Boron retention after leaching	1.29 kg/m ³
Zn	Total zinc uptake	852.4 mg
	Total zinc in wood	617.2 mg
	Zinc mass fraction in wood	0.724
	Total zinc in leachate	?
	Zinc mass fraction in leachate	?
	Mass balance	?
	Zinc retention after leaching	12.16 kg/m ³
Cu	Total copper uptake	1155 mg
	Total copper in wood	1125 mg
	Copper mass fraction in wood	0.985
	Total copper in leachate	17.61 mg
	Copper mass fraction in leachate	0.015
	Mass balance	98.93 %
	Copper retention after leaching	22.17 kg/m ³

EXAMPLE 4

5

Preparation of Impregnant

While the formulation used in this example is different from that used in Examples 1, 2 and 3, the impregnant was first prepared as that in Example 3 and then 8.9 grams of potassium fluoride were added.

10

- 1000 grams of ammonia solution (28%) was added to 1000 grams of water.
- With constant agitation using a magnetic stirrer, 222.5 grams of zinc borate were added to the diluted ammonia solution.
- The solution was heated gently at 66°C to form a clear

15

- 16 -

solution.

- 200 grams of copper sulfate were added gradually and then the solution was cooled to room temperature.
- 8.9 grams of potassium fluoride were added.

5

Preparation of Wood Blocks

The procedure used to prepare blocks is very similar to that in Examples 1 and 2.

- The numbered blocks prepared for the impregnation were:
10 066, 143, 200, 205 and 261.
- The volume and the moisture of the blocks were measured.
- The weight of the blocks was determined.

Impregnation

- 15 While the impregnation was conducted in a similar way to that in Examples 1 and 2, different vacuums were used.
 - Once a vacuum of 1.9 kPa was reached, the vacuum pump was kept running for 30 minutes, and the vacuum before flooding was also 1.9 kPa.
- 20 • Flooding was commenced under vacuum.
 - Vacuum was released to atmospheric pressure after flooding was completed.
 - Atmospheric pressure was employed for 60 minutes.
 - The solution was sucked back to the work vessel under
- 25 vacuum at the end of the pressure period.
 - Vacuum was applied to the pressure vessel containing the treated blocks.
 - After a vacuum of 2.5 kPa was reached, the vacuum was run for 30 minutes.
- 30 • The lowest vacuum reached was 2.3 kPa before the vacuum was released.
 - The weight of blocks was determined straight after the pressure treatment, and the uptake and retention of chemicals calculated. The results are as follows.

35

- 17 -

Block No.	066	143	200	205	261
Uptake (g)	7.2259	7.4066	7.2929	7.1257	7.6352
Retention (kg/m ³)	573.03	593.29	580.64	567.38	612.88

- Blocks were dried naturally in the open air.

Leaching

The leaching was carried out in a similar way to that used in Example 1 although different vacuums were used.

- The leaching was conducted as detailed in the American Wood Preserver's Association Standard E11-8.
- The blocks were impregnated with distilled water in exactly the same way as in the impregnation with preservatives.
- Once a vacuum of 0.5 kPa was reached, the vacuum pump was kept running for 30 minutes.
- Distilled water was used for the flooding.
- Vacuum was released to atmospheric pressure.
- The amount of water used was 50 ml per block, and the total amount of water used was 300 ml. The loss of water to the uptake was re-added.
- Once the leaching was commenced, the leachant was changed at intervals of 6 hours, 24 hours and every 48 hours afterwards, and the leachates were collected for analysis.

Analysis of Impregnant, Leachates and Digested Blocks after Leaching

All the analyses were carried out using techniques of AAS (Atomic Absorption Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) with the final results based on ICP analysis.

1. Analysis of impregnant

- The impregnant was diluted to an appropriate concentration that is within the working range of the

- 18 -

analytical instrument.

- The diluted impregnant was determined and the concentrations of boron, zinc and copper were 10.63g/L, 27.11g/L and 36.55g/L respectively.
- 5 • The determined concentration of the impregnant was used to calculate the mass balance.

2. *Analysis of leachates*

- 10 • The leachates were analysed directly without any further sample preparation.
- The concentrations of boron and copper in the leachates were as follows.

Sample	L1	L2	L3	L4	L5	L6	L7	L8	L9
B (ppm)	469	501	48.4	20.0	20.7	13.7	7.45	5.82	6.13
Cu (ppm)	57.0	46.2	4.32	2.78	3.61	2.87	1.99	2.20	1.69

15 3. *Analysis of digested wood blocks*

- Four out of five blocks were used for the digestion and analysis, and the other one was used for a penetration test.
- The four blocks were quantitatively powdered, homogenised and dried at 100°C for 2 hours before analysis.
- 20 • 3.0000 grams of wood powder were taken for the digestion.
- The digestion was carried out based on the American Wood Preserver's Association Standard A7-93 using nitric acid, sulfuric acid and perchloric acid.
- 25 • The solutions obtained from the digestion were analysed for boron, zinc and copper and the results are as follows.

30

- 19 -

Block No.	143	200	205	261
B in digestion solution (ppm)	61.0	40.0	47.6	53.4
Total B in each block (mg)	19.39	13.60	15.51	17.59
Zn in digestion solution (ppm)	410	333	370	467
Total Zn in each block (mg)	130.2	113.3	120.6	153.8
Cu in digestion solution (ppm)	45.0	29.7	646	1048
Total Cu in each block (mg)	134.0	86.80	252.7	345.3

Summary of Results

B	Total boron uptake	313.3 mg
	Total boron in wood	66.09 mg
	Boron mass fraction in wood	0.201
	Total boron in leachate	262.1 mg
	Boron mass fraction in leachate	0.799
	Mass balance	104.7 %
	Boron retention after leaching	1.32 kg/m ³
Zn	Total zinc uptake	798.8 mg
	Total zinc in wood	517.9 mg
	Zinc mass fraction in wood	0.648
	Total zinc in leachate	?
	Zinc mass fraction in leachate	?
	Mass balance	?
	Zinc retention after leaching	10.35 kg/m ³
Cu	Total copper uptake	1077 mg
	Total copper in wood	818.7 mg
	Copper mass fraction in wood	0.963
	Total copper in leachate	31.12 mg
	Copper mass fraction in leachate	0.037
	Mass balance	78.92 %
	Copper retention after leaching	16.35 kg/m ³

EXAMPLE 5Preparation of Impregnant

The formulation used in this example is the same as that in Example 3.

- 1000 grams of ammonia solution (28%) was added to 1000 grams of water.
- With constant agitation using a magnetic stirrer, 222.5 grams of zinc borate were added to the diluted ammonia solution.
- The solution was heated gently at 66°C to form a clear solution.
- 200 grams of copper sulfate were added gradually and then the solution was cooled to room temperature.

Preparation of Wood Blocks

The procedure used to prepare blocks is very similar to that in the other examples. Ten blocks were used in this example rather than five blocks as in the previous examples.

- The numbered blocks prepared for the impregnation were: 168, 039, 212, 125, 313, 080, 238, 299, 195 and 051.
- The volume and the moisture of the blocks were measured.
- The weight of the blocks was determined.

Impregnation

While the impregnation was conducted in a similar way to that used in the other examples, different vacuums were used.

- Once a vacuum of 1.0 kPa was reached, the vacuum pump was kept running for 30 minutes, and the vacuum before flooding was 0.6 kPa.
- Flooding was commenced under vacuum.
- Vacuum was released to atmospheric pressure after flooding completed.
- Atmospheric pressure was employed for 90 minutes.
- The solution was sucked back to the work vessel under

- 21 -

vacuum at the end of the pressure period.

- Vacuum was applied to the pressure vessel containing the treated blocks.
- After a vacuum of 1.3 kPa was reached, the vacuum was run for 30 minutes.
- The lowest vacuum reached was 1.2 kPa before the vacuum was released.
- The weight of blocks was determined straight after the pressure treatment, and the uptake and retention of chemicals calculated. The results are as follows.

Block No.	168	039	212	125	313
Uptake (g)	7.8782	8.6661	8.1115	9.0619	7.8899
Retention (kg/m ³)	631.92	701.65	644.38	720.57	622.53
Block No.	080	238	299	195	051
Uptake (g)	7.9759	9.4277	8.8812	9.3488	8.9464
Retention (kg/m ³)	639.15	739.31	696.62	738.04	695.30

- Blocks were dried naturally in the open air.

Leaching

- The leaching was carried out in a similar way to that in the other examples although different vacuums were used.
- The leaching was conducted as detailed in the American Wood Preserver's Association Standard E11-8.
 - The blocks were impregnated with distilled water in exactly the same way as in the impregnation with preservatives.
 - Once a vacuum of 0.9 kPa was reached, the vacuum pump was kept running for 30 minutes. A vacuum of 0.6 kPa was achieved before flooding.
 - Distilled water was used for the flooding.
 - Vacuum was released to atmospheric pressure.
 - The amount of water used was 50 ml per block, and the

- 22 -

total amount of water used was 500 ml. The loss of water to the uptake was re-added.

- Once the leaching was commenced, the leachant was changed at intervals of 6 hours, 24 hours and every 48 hours afterwards, and the leachates were collected for analysis.

Analysis of Impregnant, Leachates and Digested Blocks after Leaching

All the analyses were carried out using techniques of AAS (Atomic Absorption Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) with the final results based on ICP analysis.

1. *Analysis of impregnant*

- The impregnant was diluted to an appropriate concentration that is within the working range of the analytical instrument.
- The diluted impregnant was determined and the concentrations of boron, zinc and copper are 5.61g/L, 21.25g/L and 48.07g/L respectively.
- The determined concentration of the impregnant was used to calculate the mass balance.

2. *Analysis of leachates*

- The leachates were analysed directly without any further sample preparation.
- The concentrations of boron, zinc and copper in the leachates are as follows.

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Sample	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11
B (ppm)	174	186	157	80.1	48.5	32.0	22.4	15.6	11.9	9.62	7.59
Zn (ppm)	86.5	47.4	28.2	10.9	4.07	4.49	1.26	1.38	1.04	1.51	1.14
Cu (ppm)	131	113	110	59.3	26.8	18.9	5.14	2.88	1.75	2.17	1.52

3. *Analysis of digested wood blocks*

- After the penetration test, all the ten blocks were

- 23 -

quantitatively powdered, homogenised and dried at 100°C for 2 hours before analysis.

- 3.0000 grams of wood powder were taken for the digestion.
- 5 • The digestion was carried out based on the American Wood Preserver's Association Standard A7-93 using nitric acid, sulfuric acid and perchloric acid.
- The solutions obtained from the digestion were analysed for boron, zinc and copper and the results are as follows.

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Block No.	168	039	212	125	313
B in digestion solution (ppm)	38.9	40.5	39.7	50.0	35.1
Total B in each block (mg)	9.733	9.866	9.387	11.91	8.326
Zn in digestion solution (ppm)	539	593	595	632	579
Total Zn in each block (mg)	134.8	144.5	140.6	150.5	137.1
Cu in digestion solution (ppm)	1644	1813	1898	1997	1794
Total Cu in each block (mg)	411.3	441.5	448.3	475.8	425.0
Block No.	080	238	299	195	051
B in digestion solution (ppm)	40.5	43.4	41.4	52.5	49.0
Total B in each block (mg)	9.402	10.68	10.62	12.80	12.26
Zn in digestion solution (ppm)	588	626	590	635	611
Total Zn in each block (mg)	136.5	154.1	151.5	154.8	152.6
Cu in digestion solution (ppm)	1728	1807	1647	1770	1757
Total Cu in each block (mg)	401.1	444.5	422.6	431.7	439.2

Summary of Results

B	Total boron uptake	483.3 mg
	Total boron in wood	105.0 mg
	Boron mass fraction in wood	0.220
	Total boron in leachate	372.2 mg
	Boron mass fraction in leachate	0.780
	Mass balance	98.75 %
	Boron retention after leaching	0.832 kg/m ³
Zn	Total zinc uptake	1831 mg
	Total zinc in wood	1457 mg
	Zinc mass fraction in wood	0.939
	Total zinc in leachate	93.97 mg
	Zinc mass fraction in leachate	0.061
	Mass balance	84.68 %
	Zinc retention after leaching	11.55 kg/m ³
Cu	Total copper uptake	4143 mg
	Total copper in wood	4341 mg
	Copper mass fraction in wood	0.948
	Total copper in leachate	236.5 mg
	Copper mass fraction in leachate	0.052
	Mass balance	110.5 %
	Copper retention after leaching	34.41 kg/m ³

Comment

- 5 • The formulation prepared and utilised as detailed in Examples 3, 4 and 5 all contain copper. Each formulation detailed in every example to date contains zinc. Of great importance is the fact that basic (alkaline) zinc containing compounds have been found to exhibit a high degree of toxic efficacy to wood destroying organisms both in the marine and land environments. We have discovered a way of combining the efficacy of boron within a complex basic polyborate-zinc system which reduces the leaching of boron from commodities treated with this preservative composition. The efficacy of basic zinc containing compositions was

- 25 -

- never researched beyond its initial discovery. We have discovered a successful way of complementing the efficacy of boron with that of basic zinc compounds with the unexpected, unique reduction of the leaching of boron, resulting from the interaction of the preservative composition and its impregnated, soaked, brushed, sprayed or diffusion treated substrate.
- Fluorine is an important component of Example 4 in which it contributes additional synergistic efficacy.
 - The formulation utilised in Example 5 was prepared with a lower boron concentration. This constitutes one of several preservative compositions purposely formulated to result in a lower boron retention in timber and other treated commodities which are to be used above ground and especially in building, walkway, bush tracks and numerous other constructions. Especially useful in indoor environments, such compositions will constitute economic protection without any less or reduction in efficacy.

EXAMPLE 6

Preparation of Impregnant

The preservative composition was first prepared as detailed in Example 1. 1551 grams of this solution were slowly combined with 30 grams of N-alkyl tallow N dimethyl amino propyl N trimethyl ammonium dichloride in isopropanol water solution. This composition was agitated for several hours until a clear solution was produced. The solution was made up to 2000 grams, by addition of double distilled water. The pH of this composition was determined as 12.6.

Quaternary ammonium salts have long been known to exhibit high surface activity coupled with biological and fungicidal efficacy. Such complex compositions have usually been used to formulate emulsions of cationic nature at low pH. These unique properties have been retained in this complex wood preservative composition. Penetration

- 26 -

and distribution in treated timber have been enhanced and complemented by additional efficacy and boron fixation. However, boron diffusion and movement within the treated commodity has not been hindered, nor fixation rendered so efficient as to hinder efficacy. More surprising and wholly unexpected is the enhanced biocidal efficacy and composition stability in an alkaline environment.

A further very important development, relevant to this composition and previous surface activated compositions such as detailed in Example 7, is their inherent property of self-emulsification with a wide variety of oils which include, but are not limited to, petroleum derived oils, mineral oils, vegetable oils and more especially creosote oils, the latter having great wood preservation significance and limited potential for diversity of formulation and application.

Preparation of Wood Blocks

The procedure used to prepare blocks is very similar to that in the other examples. Totally ten blocks were used in this example.

- The numbered blocks prepared for the impregnation were: 218, 144, 250, 217, 258, 001, 132, 303, 274 and 226.
- The volume and the moisture of the blocks were measured.
- The weight of the blocks was determined.

Impregnation

While the impregnation was conducted in a similar way to that used in the other examples, different vacuums were used.

- Once a vacuum of 0.9 kPa was reached, the vacuum pump was kept running for 30 minutes, and the vacuum before flooding was also 0.9 kPa.
- Flooding was commenced under vacuum.
- Vacuum was released to atmospheric pressure after flooding completed.
- Atmospheric pressure was employed for 90 minutes.

- 27 -

- The solution was sucked back to the work vessel under vacuum at the end of the pressure period.
- Vacuum was applied to the pressure vessel containing the treated blocks for 30 minutes, and a vacuum of 1.9 kPa was reached before the vacuum was released.
- The weight of blocks was determined straight after the pressure treatment, and the uptake and retention of chemicals calculated. The results are as follows.

Block No.	218	144	250	217	258
Uptake (g)	9.6596	9.4843	9.6391	10.1950	8.7983
Retention (kg/m ³)	757.97	755.66	758.86	799.99	699.50
Block No.	001	132	303	274	226
Uptake (g)	9.6670	9.9522	9.2082	9.6967	10.0360
Retention (kg/m ³)	774.17	785.43	725.00	764.24	785.34

- Blocks were dried naturally in the open air.

Leaching

All blocks were dried at 108°C for 24 hours before leaching, and the leaching was carried out in a similar way to that in the other examples although different vacuums were used.

- The leaching was conducted as detailed in the American Wood Preserver's Association Standard E11-8.
- The blocks were impregnated with distilled water in the exactly same way as in the impregnation with preservatives.
- Once a vacuum of 1.5 mmHg was reached, the vacuum pump was kept running for 35 minutes. The final vacuum achieved before flooding was also 1.5 mmHg.
- The flooding was conducted under vacuum, and distilled water was used for the flooding.
- Vacuum was released to atmospheric pressure after the

- 28 -

flooding was completed.

- The amount of water used was 50 ml per block, and the total amount of water used was 500 ml. The loss of water to the uptake was re-added.
- 5 ◦ Once the leaching was commenced, the leachant was changed at the intervals of 6 hours, 24 hours and every 48 hours afterwards, and the leachates were collected for analysis.

10 Analysis of Impregnant, Leachates and Digested Blocks after Leaching

All the analyses were carried out using techniques of AAS (Atomic Absorption Spectrometry) and ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) with the final results based on ICP analysis.

1. *Analysis of impregnant*

- The impregnant was diluted to an appropriate concentration that is within the working range of the analytical instrument.
- 20 ◦ The diluted impregnant was determined and the concentrations of boron, zinc and copper are 4.43g/L, 17.07g/L and 42.32g/L respectively.
- The determined concentration of the impregnant was used to calculate the mass balance.

2. *Analysis of leachates*

- The leachates were analysed directly without any further sample preparation.
- 30 ◦ The concentrations of boron, zinc and copper in the leachates are as follows.

Sample	L1	L2	L3	L4	L5	L6	L7	L8	L9
B (ppm)	208	195	134	80.3	42.0	27.3	20.5	16.2	11.4
Zn (ppm)	85.3	62.1	38.9	18.2	7.09	5.10	2.51	2.47	2.43
Cu (ppm)	97.9	110	85.9	50.6	19.5	11.1	1.91	1.43	1.58

3. *Analysis of digested wood blocks*

- After the penetration test, all the ten blocks were quantitatively powdered, homogenised and dried at 100°C for 2 hours before analysis.
- 5 • 3.0000 grams of wood powder were taken for the digestion.
- The digestion was carried out based on the American Wood Preserver's Association Standard A7-93 using nitric acid, sulfuric acid and perchloric acid.
- 10 • The solutions obtained from the digestion were analysed for boron, zinc and copper and the results are as follows.

Block No.	218	144	250	217	258
B in digestion solution (ppm)	31.4	19.5	23.0	29.3	15.9
Total B in each block (mg)	7.487	4.789	5.683	6.942	4.266
Zn in digestion solution (ppm)	623	584	593	636	488
Total Zn in each block (mg)	149.7	143.8	146.2	156.3	131.1
Cu in digestion solution (ppm)	1647	1726	1692	1740	1465
Total Cu in each block (mg)	392.1	424.8	417.6	427.4	393.6

Block No.	001	132	303	274	226
B in digestion solution (ppm)	25.5	26.2	19.0	22.7	24.1
Total B in each block (mg)	6.059	6.588	5.121	5.799	6.074
Zn in digestion solution (ppm)	607	601	535	593	625
Total Zn in each block (mg)	144.5	151.4	144.2	151.7	157.4

- 30 -

Cu in digestion solution (ppm)	1664	1598	1455	1503	1606
Total Cu in each block (mg)	395.9	402.3	392.2	384.6	404.4

Summary of Results

B	Total boron uptake	426.8 mg
	Total boron in wood	58.81 mg
	Boron mass fraction in wood	0.138
	Total boron in leachate	367.5 mg
	Boron mass fraction in leachate	0.862
	Mass balance	99.88 %
	Boron retention after leaching	0.464 kg/m ³
Zn	Total zinc uptake	1645 mg
	Total zinc in wood	1476 mg
	Zinc mass fraction in wood	0.929
	Total zinc in leachate	112.0 mg
	Zinc mass fraction in leachate	0.071
	Mass balance	96.57 %
	Zinc retention after leaching	11.66 kg/m ³
Cu	Total copper uptake	4076 mg
	Total copper in wood	4035 mg
	Copper mass fraction in wood	0.955
	Total copper in leachate	189.9 mg
	Copper mass fraction in leachate	0.045
	Mass balance	103.6 %
	Copper retention after leaching	31.86 kg/m ³

CLAIMS:

1. A preserving composition which includes a basic zinc compound and a compound of boron.
- 5 2. A preserving composition according to claim 1 wherein the composition includes zinc ions and borate ions in an aqueous solution of ammonia.
- 10 3. A preserving composition according to claim 1 or claim 2 wherein the composition includes ions of copper.
4. A preserving composition according to claim 3 wherein the ions of copper are cupric ions.
- 15 5. A preserving composition according to claim 4 wherein the cupric ions are derived from copper sulfate.
6. A preserving composition according to any one of the preceding claims wherein the composition includes fluoride ions.
- 20 7. A preserving composition according to claim 6 wherein the fluoride ions are derived from potassium fluoride.
- 25 8. A preserving composition according to any one of the preceding claims wherein the composition includes a quaternary ammonium compound.
- 30 9. A preserving composition according to any one of the preceding claims wherein the composition comprises an aqueous solution containing from 5gms per litre to

- 32 -

saturation of borate ions and from 10gms per litre to saturation of zinc ions.

10. A method of preserving a cellulosic compound by
5 impregnating the cellulosic compound with a preserving composition according to any one of claims 1 to 9.

11. A method according to claim 10 wherein the cellulosic
compound is flooded with the preserving composition under
10 vacuum.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU01/00325

A. CLASSIFICATION OF SUBJECT MATTERInt. Cl. ⁷: B27K 3/32, 3/22, 3/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁷ AS ABOVE

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Derwent WPAT: IPC⁷ as above and boron+ and borat+**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, Y	EP 450568 B1 (Kabushiki Kaisha Koshii Preserving) 2 August 1995 Whole document	1 to 5, 8 to 11 6, 7
X, Y	EP 636461 A1 (Kabushiki Kaisha Koshii Preserving) 1 February 1995 Whole document	1 to 5, 8 to 11 6, 7
X, Y	WO 9218007 A1 (Saneish Pty. Ltd.) 29 October 1992 Whole Document	1 6, 7

☐ Further documents are listed in the continuation of Box C
 ☐ See patent family annex

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

 Date of the actual completion of the international search
 28 May 2001

Date of mailing of the international search report

30 MAY 2001

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU01/00325

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	9218007	AU	15680/92	AU	14840/92	US	5612046
EP	450568	AU	74062/91	CA	2039508	NZ	237673
		US	5207823	JP	4219201		
EP	636461	AU	68756/94	CA	2128983	JP	7088808
		NZ	264079	US	5478598		
END OF ANNEX							